Oceanic gas hydrate instability and dissociation under climate change scenarios

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[1] Global oceanic deposits of methane gas hydrate (clathrate) have been implicated as the main culprit for a repeated, remarkably rapid sequence of global warming effects that occurred during the late Quaternary period. However, the behavior of contemporary oceanic methane hydrate deposits subjected to rapid temperature changes, like those predicted under future climate change scenarios, is poorly understood, and existing studies focus on deep hydrate deposits under equilibrium conditions. In this study, we simulate the dynamic response of several types of oceanic gas hydrate accumulations to temperature changes at the seafloor and assess the potential for methane release into the ecosystem. The results suggest that while many deep hydrate deposits are indeed stable under the influence of rapid seafloor temperature variations, shallow deposits, such as those found in arctic regions or in the Gulf of Mexico, can undergo rapid dissociation and produce significant carbon fluxes over a period of decades. **Citation:** Reagan, M. T., and G. J. Moridis (2007), Oceanic gas hydrate instability and dissociation under climate change scenarios, *Geophys. Res. Lett.*, *34*, L22709, doi:10.1029/2007GL031671.

[2] Gas hydrates are solid crystalline compounds in which gas molecules are lodged within the clathrate crystal lattice [*Sloan*, 1998]. Natural gas hydrate deposits occur in geologic settings where the necessary low temperatures and high pressures exist for their formation and stability. Initial investigations estimated the total amount of methane hydrate currently residing in the deep ocean and along continental margins, beginning with an early "consensus value" of 10,000 gigatons (Gt, 20×10^{15} m^3 STP) of methane carbon [*Gornitz and Fung*, 1994; *Holbrook et al.*, 1996; *Kvenvolden*, 1999; *Borowski*, 2004] that has narrowed over time to 500 to 2,500 Gt (1 to 5×10^{15} m^3 STP) [*Milkov*, 2004]. Recently, two studies accounting for the contribution of organic matter decomposition and the effect of mass transport have produced different results— one yielding an upper estimate of 27,300 Gt of methane in hydrate along continental margins (74,400 Gt globally) [*Klauda and Sandler*, 2005] and the other a lower estimate of 3,000 Gt of methane in hydrate and 2,000 Gt of gaseous methane [*Buffett and Archer*, 2004]. The latter study also suggests that 55% of the ocean floor between 500 m to 3000 m is able to contain some methane in the underlying sediment column under current climatic conditions.

[3] In oceanic deposits, the depth at which hydrates remain stable depends on the pressure (as imposed by the water depth) and the temperature. Figure 1 presents a general schematic of the gas hydrate stability zone (GHSZ), geothermal gradient, and the corresponding hydrate phase boundary (at equilibrium) for oceanic hydrates. An increase in water temperature at the seafloor (represented by a shift from temperature profile 1 to profile 2) changes the extent of the GHSZ (from the area encompassed by zones A + B to zone B). Such a shift could induce hydrate dissociation and lead to methane release. The rate of release would be significantly enhanced in cases of sediment slope failure, sliding, or collapse [*Dickens et al.*, 1995]. Deep ocean surveys have found pockmarks and other structures that indicate large fluid releases at the seafloor in the past [*Hovland et al.*, 2005], and computational studies show the potential for hydrate instability under warming conditions [*Buffett and Archer*, 2004; *Milkov and Sassen*, 2003; *Archer and Buffett*, 2005].

[4] The dissociation of accumulated hydrate deposits and the rapid release of large quantities of methane, a powerful greenhouse gas (some 26 times more powerful than CO_2), could have dramatic climatic consequences, leading to further atmospheric and oceanic warming through accelerated decomposition of the remaining hydrates. This positive-feedback mechanism has been proposed as a significant contributor to rapid and significant climate changes in the late Quaternary period [*Kennett et al.*, 2000; *Brook et al.*, 1996; *Severinghaus et al.*, 1998; *Behl et al.*, 2003]. The Clathrate Gun Hypothesis [*Kennett et al.*, 2002] proposes that past increases in water temperatures near the seafloor may have induced such a large-scale dissociation, with the methane spike and isotopic anomalies reflected in polar ice cores and in benthic foraminifera. This hypothesis has been challenged by other interpretations of the paleoclimatic data [*Nisbet*, 2002; *Sowers*, 2006] as well as steady-state simulations suggesting that deep (>1000 m) hydrates are stable [*Xu and Lowell*, 2001]. With contemporary concerns about increasing global temperatures, the possibility of this mechanism occurring in the near future must be investigated.

[5] Significant gaps still exist in our understanding of the dynamic response of oceanic hydrates to changes in ocean temperature and the resulting gas and aqueous transport through benthic sediments into the water column. Hydrates found in the deep ocean are stable due to pressures well above and temperatures well below those defining the hydrate phase boundary. These deep deposits have been the primary focus of previous investigations [*Klauda and Sandler*, 2005; *Xu and Lowell*, 2001]. Stable hydrates also exist in shallower regions, with phase diagrams and ocean drilling evidence indicating that the top of the GHSZ lies below 300 m depth on the continental shelf in cold arctic

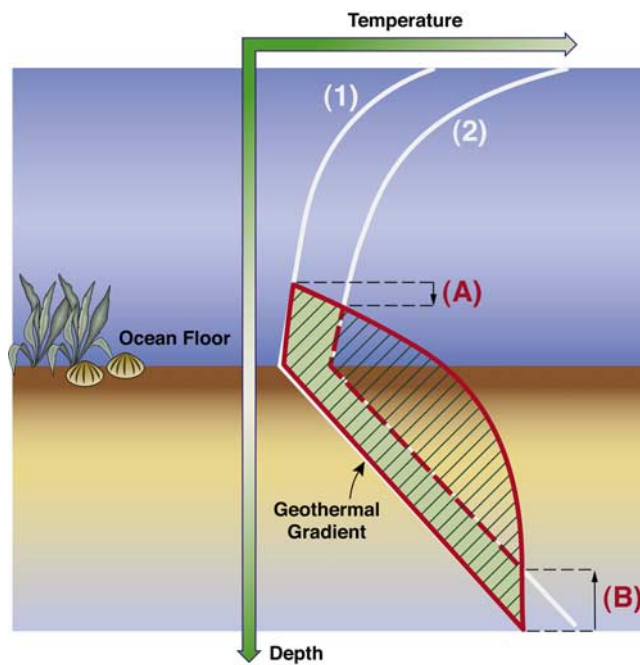[1]Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, USA.

Figure 1. Schematic of the gas hydrate stability zone in the seafloor environment (not to scale). In this example, the top of the gas hydrate stability zone (GHSZ) is well above the seafloor; however, the boundary may exist above, at, or below the seafloor depending on local pressure and temperature conditions. Increasing temperatures (temperature profile 1 to temperature profile 2) lowers the position of the top of the GHSZ (A) and raises the position of the bottom of the GHSZ (B), as the zone of hydrate stability is defined by the intersection of the temperature profile with the phase envelope.

waters and below 440 m in the warmer Gulf of Mexico [*Milkov and Sassen*, 2001]. Shallow deposits would be more affected by changes in ocean temperature, as decreasing pressure decreases the temperature range over which hydrates are stable. For example, previous studies indicate that a temperature change of 4°C could result in a 30% thinning of the GHSZ in the Gulf of Mexico [*Milkov and Sassen*, 2003]. An additional issue to be considered is the effect of benthic biogeochemistry as a function of methane flux and fluid velocity at the seafloor. Communities of methane-consuming, chemosynthetic fauna have been found atop gas hydrate deposits [*Sassen et al.*, 1999] and biochemical reactions within sediments can oxidize methane to CO_2 or sequester released carbon as solid carbonate [*Boetius and Suess*, 2004; *Luff et al.*, 2005].

[6] We evaluate the stability and dynamic behavior of hydrates subjected to century-scale temperature variations using the TOUGH + HYDRATE code [*Moridis et al.*, 2005], which models the nonisothermal hydration reaction, phase behavior and flow of fluids and heat under conditions typical of natural CH_4-hydrate deposits in complex geologic media [*Moridis et al.*, 2005; *Moridis and Kowalsky*, 2005; *Moridis and Sloan*, 2007]. TOUGH + HYDRATE can handle any combination of hydrate dissociation processes. We simulate three types of hydrate accumulations under three ocean warming scenarios. The first case involves

deep, cold hydrate deposits at a depth of 1000 m, with an initial seafloor temperature of $T_{i,s} = 4°C$, an initial hydrate saturation of $S_H = 0.10$, and a typical deep-ocean geothermal gradient of 3.5°C/100 m [*Xu and Lowell*, 2001]. These conditions indicate stable hydrate, with the GHSZ well above the seafloor. The second case involves warm, low-saturation hydrate deposits at 570 m depth, $T_{i,s} = 6°C$, $S_H = 0.03$, and a geothermal gradient of 2.8°C/100 m. This case is representative of Gulf of Mexico deposits [*Milkov and Sassen*, 2001], with the top of the GHSZ near the seafloor. The third case describes shallow, cold hydrate deposits at 320 m depth, $T_{i,s} = 0.4°C$, $S_H = 0.10$, representative of conditions on the arctic continental shelf, where the top of the GHSZ is located at the seafloor.

[7] The simulations use a vertical, 1-D domain representing the sediment column from the seafloor downward, with a constant pressure maintained at the top of the sediment column. The initial condition involves a hydrostatic pressure distribution, a constant geothermal gradient, and uniform hydrate saturation in the sediment column within the GHSZ. The intrinsic permeability for this base case, $k = 1$ mD, is within the reported range of oceanic sediments [*Ginsburg and Soloviev*, 1998] and represents the more common stratigraphic deposits [*Milkov*, 2004; *Moridis and Sloan*, 2007], in contrast to the less common, more permeable, and often more saturated structural deposits near sites of active methane seepage and/or venting. The porosity $\phi = 0.3$ is typical for unconsolidated marine sediments near the mudline [*Ginsburg and Soloviev*, 1998]. For the dynamic simulations, constant pressure is maintained at the top of the sediment column, while the temperature at the top boundary, representing the overlying water, is varied. The top of the sediment column is bounded by an open boundary representing heat and mass transfer between the sediment and the bulk ocean. The sediment column below the GHSZ is modeled to 360 m below the seafloor, well beyond the reach of temperature propagation over the simulated time. Results from recent simulations coupling ocean circulation, atmospheric circulation, and atmospheric chemistry (CCSM special overview issue, *Journal of Climate*, *19*(11), 2006) indicate that, under current climate conditions and a 1%/yr increase in atmospheric CO_2, the temperature at the seafloor would rise by 1°C over the next 100 yr, and possibly by another 3°C in the following century. Consequently, we choose simple linear temperature increases of 1, 3, and 5°C over a 100 yr simulation period, varying the temperature at the upper boundary to represent changes in the bulk ocean temperature above the seafloor. The pressure at the upper boundary is held constant, reflecting a constant depth, as unrealistically large sea level increases would be required to compensate for the smallest postulated changes in temperature. The system evolves dynamically in time. We record methane fluxes (Figure 2) and fluid flow velocities through the upper boundary, as well as the pressure, temperature, and phase saturation profiles at regular intervals.

[8] Deep, cold hydrates at 1000 m depth are stable when subjected to all three temperature change scenarios. No gas escapes from the top of the deposit within the 100 yr observation window, and aqueous fluxes are insignificant. The temperature and phase saturation profiles for the 3°C scenario (Figure 3a) show only limited dissociation is seen at the lower hydrate boundary, as the bottom of the GHSZ
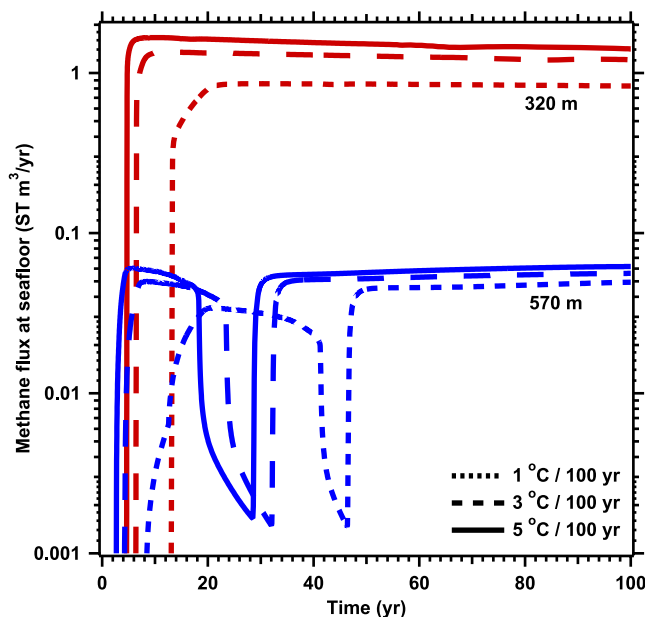
Figure 2. Total methane flux at the seafloor (top of the simulated 1-D sediment column) vs. time for two locations (320 m and 570 m depths) and three temperature-change scenarios (linear increases of +1°C, +3°C, and +5°C over 100 yr). Total methane flux includes methane transported in the gas phase as well as methane dissolved in pore water. Note the two flux regimes for the 570 m location: the initial release of methane is entirely dissolved in the aqueous phase, and the second, continuing release is primarily gas.

moves upward in response to the shifted temperature gradient. The simulation indicates that hydrate saturation increases just above the newly formed free gas zone, as rising gas re-enters the GHSZ and combines with available water to form new secondary hydrate. Induced fluid velocities at the top of the sediment column do not exceed 0.44 cm/yr within the first 100 yr. Additional simulations (not shown) indicate that an extreme case of a 10°C/100 yr excursion is needed before any gas escapes the sediment.

[9] A warm, thin, sparse hydrate deposit at 570 m depth exhibits a stronger response to a rise in temperature. Initially, methane dissolved in pore water is released for periods of 20 yr (+5°C), 22 yr (+3°C), and 44 yr (+1°C). This fluid flow is driven by the rapid dissociation of the hydrate and formation of methane gas in the previously water-saturated hydrate layer. Aqueous methane flux at the top of the sediment column (reported in m^3 of CH_4 at standard temperature and pressure) peaks at rates of 0.060 ST $m^3/yr/m^2$ (+5°C), 0.050 ST $m^3/yr/m^2$ (+3°C), and 0.034 ST $m^3/yr/m^2$ (+1°C) with corresponding aqueous flow velocities of 7.6, 6.3, and 4.3 cm/yr, respectively. There is a brief (3–5 yr) reduction in both methane flux and fluid flow as the hydrate is exhausted and gas formation declines. Then, dissociation-derived methane gas reaching the top of the sediment column induces fluxes of 0.062 ST $m^3/yr/m^2$ (+5°C), 0.056 ST $m^3/yr/m^2$ (+3°C), and 0.049 ST $m^3/yr/m^2$ (+1°C) at $t = 100$ yr. Both the aqueous and gaseous fluxes are within the range of integrated anaerobic methane oxidation rates calculated for benthic sediments [*Luff et al.*, 2005] and below the rates of methane consumption by chemosynthetic communities near active venting sites [*Boetius and Suess*, 2004]. The hydrate deposit dissociates from both the top (Figure 3b), as the temperature
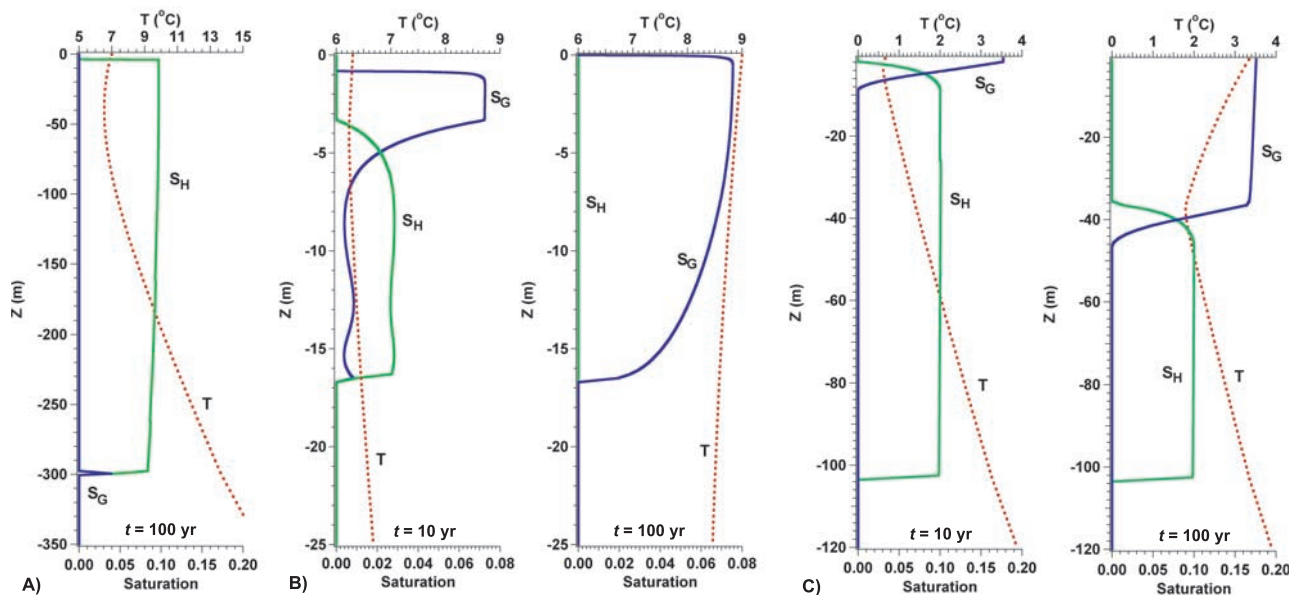

Figure 3. Temperature, hydrate saturation (S_H), and gas saturation (S_G) profiles for the three locations for the +3°C temperature change scenario. (a) Case A shows the 1000 m deposit at $t = 100$ yr. Free gas is only seen at the base of the GHSZ. (b) Case B shows the 570 m deposit at $t = 10$ yr and $t = 100$ yr. No solid hydrate remains at $t = 100$ yr. (c) Case C shows the 320 m deposit at $t = 10$ yr and $t = 100$ yr. This thick deposit dissociates primarily from the top, and considerable hydrate remains after 100 yr. Approximately 200 yr of additional time is required for the temperature change to propagate to the bottom of the deposit.

change at the seafloor lowers the upper boundary of the GHSZ, and from the bottom. At $t = 100$ yr, we see only gas ascending through the column toward the seafloor.

[10] A shallow, cold hydrate deposit at 320 m exhibits the strongest reaction to a rise in temperature. Release of methane begins primarily in the gaseous phase, peaking at 1.7 (+5°C) ST m^3/yr/m^2, 1.3 (+3°C), and 0.86 (+1°C). Pore water velocities at the seafloor peak at 20.2 cm/yr at 4.7 yr (5°C), 14.4 cm/yr at 6.6 yr (3°C), and 7.3 cm/yr at 13 yr (1°C), followed by decreases to 7.1 cm/yr, 5.7 cm/yr, and 3.6 cm/yr, respectively, at $t = 100$ yr. These methane fluxes are 5 to 8 times greater than rates of benthic sediment methane oxidation [*Luff et al.*, 2005], and the primary method of methane transport is in the gas phase. Chemosynthetic organisms in sediments have been shown to consume on the order of 1.0 ST m^3/yr/m^3 methane equivalent [*Boetius and Suess*, 2004]. However, it is not known how the seafloor ecosystem would respond to surges in methane emission over short timescales. The cumulative mass of methane entering the top of the sediment column over the 100-year timeframe under these conditions would be 71.8 kg/m^2 (+1°C), 119 kg/m^2 (+3°C), and 145 kg/m^2 (+5°C). The hydrate zone dissociates from the top (Figure 3c), as heat flows downward from the warming seafloor, and the release of methane gas continues through the 100 yr mark, at which point the top 36 m of the hydrate deposit has completely dissociated. Figure 3c also shows a dissociation front progressing downward through the hydrate-bearing sediments, reaching a depth of 46 m at $t = 100$ yr. The recession of this front is regulated by (1) the endothermic nature of the hydrate dissociation reaction, (2) the flux of heat downward from the seafloor, and (3) the upward transport of fluids. Further simulations indicate that, with no additional change in seafloor temperature, the dissociation front reaches the bottom of the hydrate-bearing layer and exhausts the hydrate at $t = 300$ yr.

[11] These results confirm the stability of deep ocean hydrates, but indicate that the greatest potential impact of ocean warming would be on shallow hydrate deposits, particularly in arctic regions. In such regions, temperature rises are expected to be more pronounced (CCSM special overview issue, *Journal of Climate*, 19(11), 2006) and the deposits are both thicker and more readily destabilized. To assess the full consequences of rapid release for all types of shallow deposits, and to estimate the quantity of carbon that may reach the atmosphere, we need (1) a detailed inventory of gas hydrate deposits in the regions of concern, particularly the arctic continental shelf, and (2) coupled modeling, involving dissociation, transport, thermal, and biogeochemical processes, to assess the short-term response of CH$_4$-fueled chemosynthetic communities to methane releases. Further simulations could provide a quantitative estimate of the potential of carbon release from hydrates, and provide a source term to global climate models that can yield a prediction of the possible consequences of clathrate decomposition on global climate.

Notation

T temperature, °C
S_H hydrate saturation
S_G gas saturation
k   permeability, mD (10^{-15} m^2)
ϕ porosity

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